ON THE DEPENDENCE OF THE TIME OF RELAXATION OF NITROBENZENE IN SOLUTIONS IN NON POLAR SOLVENTS ON THE VISCOSITY OF THE SOLUTIONS

J. BHATTACHARYYA, (Miss) B. SINHA, S. B. ROY AND G. S. KASTHA

OPTICS DEPARTMENT, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE CALCUTTA-32

(*Received July 7, 1964*)

ABSTRACT. The dielectric loss due to absorption of microwaves of frequency 38.8 KMc/s in dilute solutions of CCl_4, C_6H_6, C_6H_{14} at different temperatures and in mixed solvents of paraffin+CCl_4, paraffin+C_6H_6 and paraffin+C_6H_{14} at constant temperature but at different viscosities have been studied. It has been found that the values of tan δ or T tan δ at different viscosities in solutions in pure solvents or in mixed solvents lie on smooth curves. The values of tan δ for the same value of viscosity in solution in pure and in mixed solvents, agree with each other, so long the viscosity remains within 1.3 c.p. Within this limit the time of relaxation is proportional to viscosity of the solution. It is concluded that within certain limitations the dependence of tan δ on the viscosity in a dilute solution may be expressed by the Debye equation.

Incidentally, a method has been suggested for the determination of dipole moment of polar molecule in solution in nonpolar solvent when a maximum in the value of tan δ could not be obtained.

INTRODUCTION

The dielectric loss accompanying absorption of microwaves of wavelength 3-cm and 1.25 cm in dilute solutions of nitrobenzene and of some other polar organic compounds in C_6H_6 and CCl_4 and in mixed solvents of high viscosity paraffin and a nonpolar solvent such as CCl_4, C_6H_6, C_6H_{14} and CS_2 have been studied by many workers (Whiffen and Thompson, 1946; Hall *et al.*, 1946; Cripwell and Sutherland 1946; Chau *et al.*, 1957 and Rajan, 1957). From these results it was concluded that though the Debye expression for dielectric loss in dilute solutions of polar compounds in nonpolar solvents is fairly obeyed, the Debye relation connecting the time of relaxation with the macroscopic viscosity of the solution and the radius of the rotor does not hold good (Whiffen and Thompson, 1946; Jackson and Powles, 1946).

The effect of viscosity on the dielectric loss was studied by Jackson and Powles (1946) who found that in the case of solution of benzophenone in high viscosity paraffin the whole loss curve obtained by varying the frequency of microwave radiation becomes broader and also the frequency at which maximum loss

occurs is shifted towards lower frequency value in comparison with those obtained in the case of dilute solution of benzophenone in benzene.

Hall *et al.* (1946) studied the absorption of microwaves of wavelength 3-cm in solutions of nitrobenzene in mixed solvents of paraffin+CCl_4, paraffin+C_6H_6 and paraffin+C_6H_{14} with variation of viscosity and found that in each case maximum attenuation occurs at such viscosity-value of the solution which increases as the viscosity of the low viscosity component in the mixed solvents decreases. Whiffen (1946) suggested that all these results might indicate that the Debye equation for loss tangent does not hold in the case of solution whose viscosity is greater than 1.5 c.p.

In order to determine how the value of loss tangent and the time of relaxation are related with the viscosity of the solution, it would be necessary to make a comparative study of the variation of dielectric loss with the variation of viscosity produced either by changing the temperature of the solution or by mixing with the solution high viscosity paraffin in different proportions. With this object, the absorption of microwaves in the frequency region 35 Kmc/s—39Kmc/s by dilute solutions of nitrobenzene in various nonpolar solvents at different temperatures and different viscosities has been studied and the results obtained have been discussed in the present paper.

EXPERIMENTAL

Experimental arrangements for studying the absorption of microwaves in solutions at different temperatures and at different viscosities are shown in the schematic diagram, figure I. Microwave power from the signal generator (Model E.H.F. G3540—1 of Polarad Electronics Corporation) is passed through a U-shaped absorption cell containing the solution, the temperature of which can

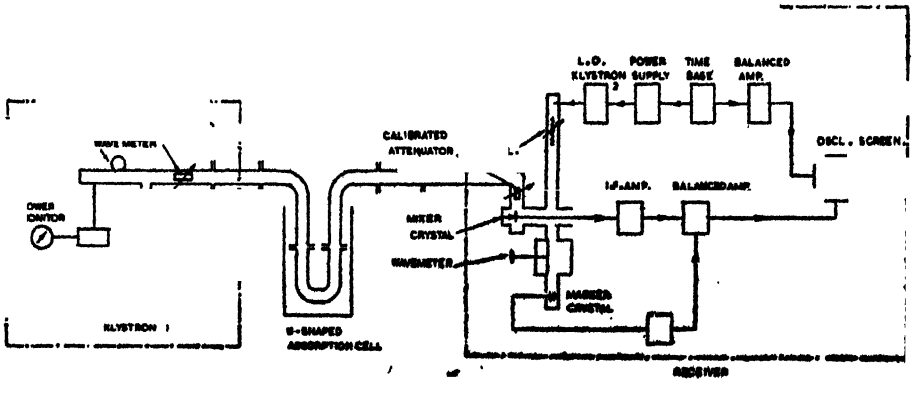

Fig. 1. Schematic diagram of the experimental arrangements for measuring dielectric loss.

be raised or lowered to any desired value by placing the cell in a suitable hot or cold bath. The signal after absorption in the cell is detected by a superheterodyne receiver having a sensitivity of 55 db. (Microwave spectrum analyzer model

SA40 of Applied Dynamics Corporation). The frequency of the local oscillator is swept by a 20c/s saw-tooth volatge so that it can follow the signal. The same saw-tooth voltage is used for the horizontal deflecting plates of the scope. After about half an hour of switching on the instruments the signal on the screen becomes steady. The constancy in the microwave power of the signal source is seen from the thermistor bridge power monitor. The frequency of the signal is measured with an accuracy of 0.1% by means of absorption type wavemeters incorporated in the signal generator as well as in the receiver. With the pure solvent (2 cc) in the absorption cell, the calibrated attenuator on the instruments are adjusted to give a full scale deflection on the scope. With the solution (2 c.c.) in the cell, the attenuators are again adjusted for the same full scale deflection. The difference in the readings of the attenuators gives directly the loss of microwave power in *db* due to absorption in solution with an accuracy of 0.25 *db*. The distance of the absorption cell is about 90 cm. either from the signal generator or from the receiver so that the temperature variations of the cell can not reach them. Mica windows are used in the absorption cell to prevent the vapour of the solution from entering the signal generator or the receiver. The validity of the Beer's Law is seen from the linear change in the amount of absorption either with variation of the concentration of the solution or of the path length. This also indicates that the formation of stationary waves, if any, is negligible.

Chemically pure nitrobenzene, used as solute and CCl_4, C_6H_6, C_6H_{14} used as solvents were distilled repeatedly and thoroughly dried before being used in the investigations. The dielectric loss of the solvents in a path length of 24 cm was measured and found to be negligible. Medical paraffin, which also showed negligible absorption in the same path length, was used to produce mixed solvents of variable viscosity. The values of dielectric constants and viscosities of the solvents were taken from the International Critical Tables. The viscosities of paraffin and of the mixed solvents at room temperature were determined experimentally.

RESULTS

Calculation of loss tangent (tan δ)

The observed loss of microwave power (ϕ) in *db* due to absorption of microwaves in dilute solutions of nitrobenzene in various solvents is related to the value of attenuation coefficient ψ (Whiffen, 1946) by the relation $\psi = \frac{.2303}{L}\phi$ where L is the length of absorbing path in cm. The values were then converted into tan δ-values with the help of the relations given by Jackson (1946) and by Whiffen and Thompson (1946). In calculating the tan δ-values the value of real dielectric constant ϵ of the solution was taken to be the same as that of the solvent and its variation with temperature was neglected. In the case of mixed solvents, Paraffin+C_6H_6, Paraffin+CCl_4, Paraffin+C_6H_{14}, the value of ϵ was taken to be

2.2 because the dielectric constant of paraffin is 2.2 and those of pure solvents are about 2 in all cases. The estimated error in tan δ-values is about 5%. These values are given in Tables I, II and III.

TABLE IA

1.95×10^{-4} moles/cc of nitrobenzene in CCl_4. Volume of solution in the cell 2cc

Temp (abs)	tan δ	T tan δ	$\tau \times 10^{12}$ sec	$\tau \times 10^{12}$ sec (lit)	$\eta \times 10^3$ poise	$\frac{\tau}{\eta} \times 10^{10}$
262	.03	7.89	25.6		—	—
274	.036	9.86	20.05		13.3	15.0
283	.038	10.75	18.3		12.5	14.64
294	.041	12.05	16.1	15.2[a]	9.52	16.9
				14.0[b]		
303	.047	14.24	13.2		8.25	16
313	.05	15.65	11.8		7.50	15.73
323	.051	16.47	10.9		6.56	16.6
333	.053	17.65	9.8		5.75	17
343	.056	19.21	9.06		5.24	17.2

a. Whiffen (1950)

b. Chau, Fevre and Tardif (1957)

TABLE IB

1.95×10^{-4} moles/cc of nitrobenzene in CCl_4+paraffin
Volume = 2cc Temperature = 30°C

Percentage of paraffin	tan δ	T tan δ	$\tau \times 10^{12}$ sec	$\eta \times 10^3$ poise	$\frac{\tau}{\eta} \times 10^{10}$
0%	.0458	13.88	13.60	8.25	16.48
10%	.0413	12.51	15.40	10.10	15.24
20%	.0362	10.97	17.85	11.57	15.42
100%	.029	8.79	22.80	164.7	1.38

TABLE IIA

1.95×10^{-4} moles/cc of nitrobenzene in benzene
Volume of solution in the cell = 2 cc

Temp (abs)	tan δ	T tan δ	$\tau \times 10^{12}$ sec	$\tau \times 10^{12}$ sec lit	$\eta \times 10^{3}$ poise	$\frac{\tau}{\eta} \times 10^{10}$
267	.0298	7.95	25			
274	.0397	10.82	17.9		9.00	19.9
285	.048	13.68	13.31		7.55	18
				11.5[a]		
293	.0514	15.06	12.31	11.6[b]	6.47	19
				13.0[c]		
				11.0[d]		
				12.3[e]		
303	.054	16.36	11.13		5.60	19.9
314	.056	17.58	10.8		4.90	22
323	.0578	18.67	9.3		4.36	21.3
333	.0606	20.18	8.09		3.89	20.8
347	.0646	22.42	6.37		3.36	18.95

a—Jackson and Powles (1946)
b—Whiffen and Thompson (1946)
c—Cripwell and Sutherland (1946)
d—Chau, Fevre and Tardif (1957)
e—Gopala Krishna (1957)

TABLE IIB

1.95×10^{-4} moles/cc of nitrobenzene in benzene+paraffin
Volume of solution in the cell 2cc. Temperature = 30°C

Percentage of paraffin	tan δ	T tan δ	$\tau \times 10^{12}$ sec	$\eta \times 10^{3}$ poise	$\frac{\tau}{\eta} \times 10^{10}$
0%	.0536	16.24	11.2	5.61	20
20%	.0493	14.94	12.5	7.69	16.25
40%	.041	12.42	15.52	12.05	12.88
60%	.035	10.61	18.5	19.57	9.45
100%	.029	8.79	22.8	164.7	1.38

TABLE IIIA

1.95×10^{-4} moles/cc of nitrobenzene in hexane
Volume of solution in the cell=2 cc

Temp (abs)	tanδ	T tan η	$\tau \times 10^{12}$ sec	$\delta \times 10^{12}$ sec (lit)	$\tau \times 10^{3}$ poise	$\tau/\eta \times 10^{10}$
265	.062	16.43	9.70			
274	.072	19.73	7.17	6.8[a]	3.89	18.43
303	.075	22.79	4.53		2.89	15.67

[a]Chau, Fevere and Tardif (1957)

TABLE IIIB

1.95×10^{-4} moles/cc of nitrobenzene in hexane+paraffin
Volume of solution in the cell = 2cc Temperature = 30°C

Percentage of paraffin	tanδ	T tanδ	$\tau \times 10^{12}$ sec	$\eta \times 10^{3}$ poise	$\tau/\eta \times 10^{10}$
0.%	.075	21.57	4.53	2.89	15.67
20%	.064	19.39	8.7	5.25	16.5
40%	.0508	15.39	11.99	9.91	12.09
60%	.0469	14.21	13.23	16.93	7.8
80%	.0369	11.18	17.48	44.45	3.93
100%	.029	8.79	22.8	164.7	1.38

From the data given by Cripwell and Sutherland (1946) for tan δ-value (reduced to a theoretical concentration of 1 gm.mol/100 c.c.) in the case of solution of nitrobenzene in benzene at about 20°C for two wavelengths 3.25 cm and 1.25 cm, the value of tan δ for the same concentration at the wavelength 7.7 mm was calculated and found to be 2.50. This agrees well with the tan δ-value 2.63 obtained for the same theoretical concentration in the present investigation.

Calculation of time of relaxation (τ)

The expression for loss tangent in the case of dilute solution of polar molecules in nonpolar solvent is given by the Debye equation

$$\tan \delta = \frac{(\epsilon+2)^2}{\epsilon} \cdot \frac{4\pi N c \mu^2}{27kT} \cdot \frac{\omega\tau}{1+\omega^2\tau^2} \qquad \ldots (1)$$

where the various symbols have their usual meaning. For the calculation of τ with the help of the above equation from the observed values of tan δ, the value of μ is required. In the present case as the maximum value of tan δ was not obtained, the value of μ. could not be determined independently. So μ was taken as 3.98D from the literature (*c.f.* Jackson and Powles, 1946; Cripwell and Sutherland, 1946). The calculated values of τ along with the macroscopic viscosity η are given in Tables I, II and III. The τ-values reported by other workers have been included in the Tables for comparison. The last column of each table contains the values of τ/η.

DISCUSSION

(a) *Variation of loss tangent with viscosity*

The values of tan δ and T tan δ obtained in the case of each of the solutions have been plotted separately against the log η values of the respective solutions and are shown in Figs. 2a, 2b and 2c. It can be seen that in all the cases points corresponding to the values of tan δ and T tan δ at different values of viscosity obtained either by changing the temperature of the solution or by varying the proportion of paraffin added to the solution lie on smooth curves. It is also seen that the values of T tan δ decreases almost exponentially with increase in the value of log η. This is also evident from the near constancy in the values of T tan $\delta.\eta$ given in Tables I and II. However, in the case of the solutions in mixed solvents, T tan δ-values do not decrease as rapidly with increase of viscosity

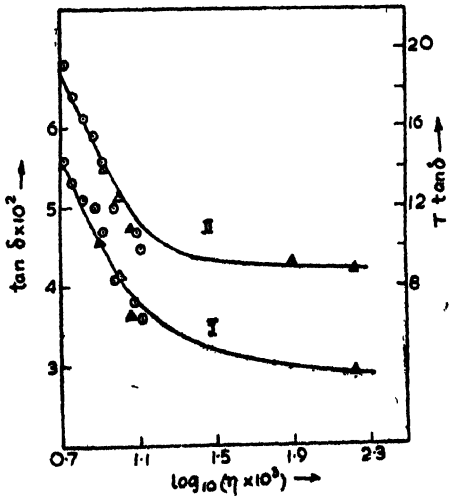

Fig. 2a. Curve I. Variation of loss tangent with logarithm of viscosity for solutions of nitrobenzene in CCl_4 and in CCl_4 + paraffin.

Curve II Dependence of T tan δ on log η for the same solutions.

Δ Points for variation of temperature

O Points for variation of viscosity at constant temperatute.

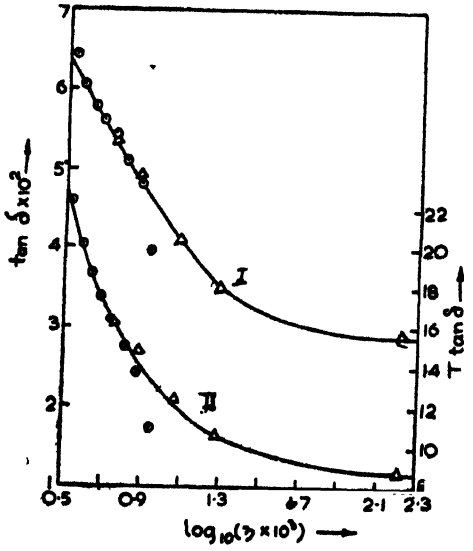

Fig. 2b. Curve I Variation of loss tangent with logarithm of viscosity for solutions of nitrobenzene in benzene and in benzene+paraffin.

Curve II Dependence of T tan δ on log η for the same solutions.

Δ Points for variation of temperature.

O Points for variation of viscosity at constant temperature.

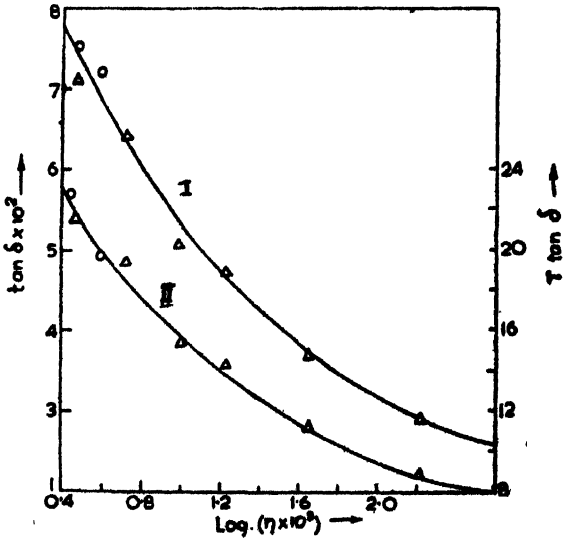

Fig. 2c. Curve I Variation of loss tangent with logarithm of viscosity for solutions of nitrobenzene in hexane and in hexane+paraffin.

Curve II Dependence of T tan δ on log η for the same solutions.

O Points for variation of temperature.

Δ Points for variation of viscosity at constant temperature.

as would be expected if the same exponential law would hold, but instead, the values of T tan δ tend to reach constant limiting values. It may be noted that so long the viscosity of the solution remains within a certain value which is about 1.3 c.p. in the present case, the variation in the value of tan δ or T tan δ by varying the value of η does not depend on whether the change of η is effected by changing the temperature of the solution or the concentration of paraffin in the solution.

(b) *Relation between τ and η*

Whiffen and Thompson (1946) discussed the variation of τ and η with temperature in terms of the expressions

$$\left.\begin{aligned}\tau &= A \cdot e^{E_\tau/RT} \\ \eta &= B \cdot e^{E_\eta/RT}\end{aligned}\right\} \quad \ldots \quad (2)$$

where A and B are constants. Molar activation energy for dielectric relaxation E_τ and that for viscous flow E_η have been measured from the inclinations of the straight line plots of log τ and log η against $1/T$ (Figs. 3a, 3b) in the case of solutions of nitrobenzene in CCl_4 and C_6H_6. The values of E_τ and E_η are given in Table IV. E_τ-value in hexane solution was calculated from the τ-values at two temperatures.

TABLE IV

Solution in	E_τ in K.Cal/mole	E_η in K.Cal/mole	E_τ/E_η
CCl_4	2.25	2.44	0.92
C_6H_6	2.56	2.53	1.01
C_6H_{14}	2.08	1.84	1.13

The closeness in the values of E_τ and E_η in all cases suggests that there might be a simple relation between τ and η which, with the help of the above two equations, may be expressed as

$$\tau/\eta = D \cdot e^{(E_\tau - E)/R\eta T} \text{ or } \tau = \alpha \cdot \eta^{E_\tau/E_\eta} \quad (3)$$

where D and α are constants. The value of τ will increase, remain constant or decrease with increase of temperature or decrease of viscosity according as $E_\tau \lessgtr E_\eta$. This is found to be approximately true from the τ/η-values given in Tables I, II and III.

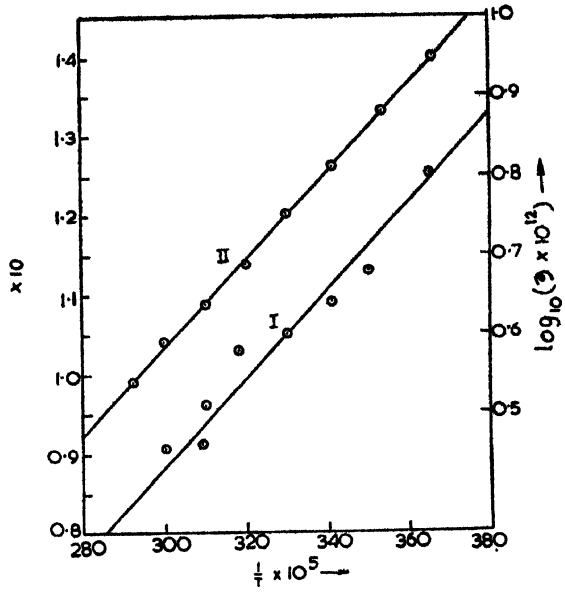

Fig. 3a. Curve I Plot of $\log \tau$ vs $1/T$ for solution of nitrobenzene in CCl_4
Curve II Plot of $\log \eta$ vs $1/T$ for CCl_4.

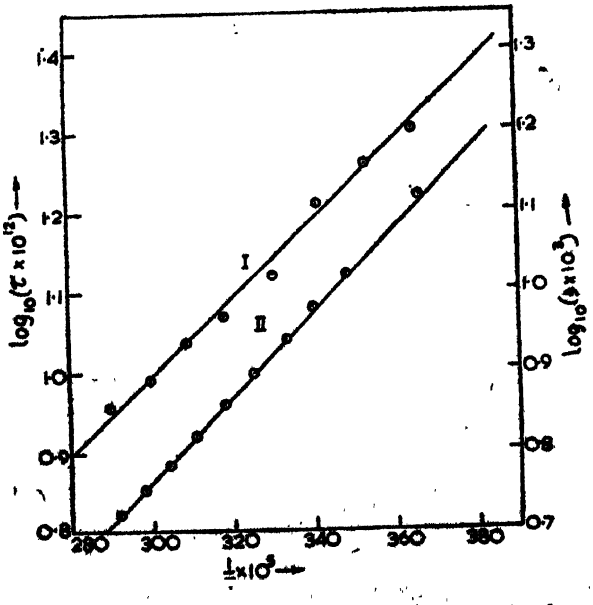

Fig. 3b. Curve I Plot of $\log \tau$ vs $1/T$ for solution of nitrobenzene in benzene.
Curve II Plot of $\log \eta$ vs $1/T$ for benzene.

If the relation (3) holds, the plot of log τ vs log η would be a straight line with an inclination E_τ/E_η. Actually, the plots of log τ vs logη (Figs. 4a, 4b and 4c) are almost linear upto certain values of η and the values of the inclination E_τ/E_η agree well with the ratios of E_τ and E_η determined separately. Because of the

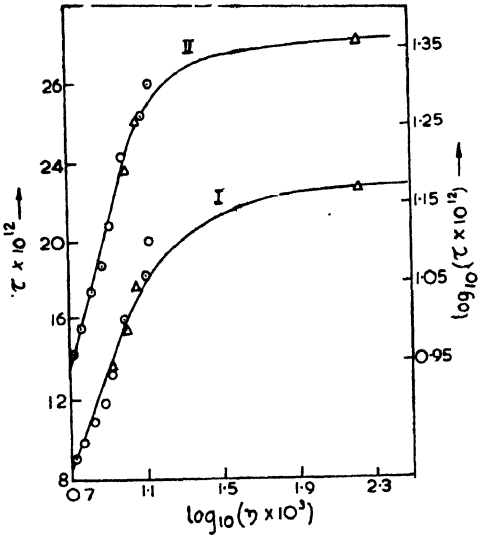

Fig. 4a Curve I Graph of τ vs log η for solutions of nitrobenzene in CCl_4 and in CCl_4 + paraffin.

Curve II Graph of log τ vs log η for the same solutions.

O Points for variation of temperature.

Δ Points for variation of viscosity at constant temperature.

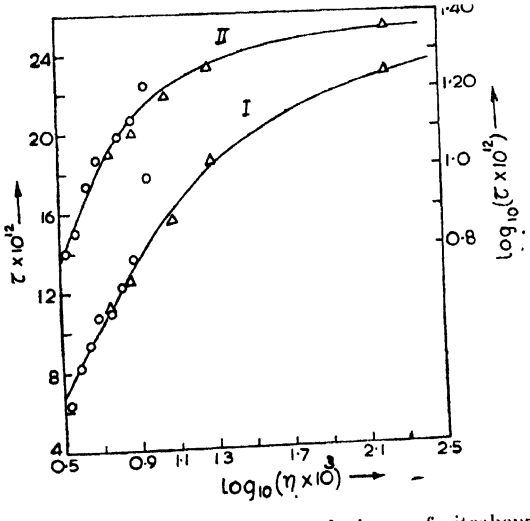

Fig. 4b. Curve I Graph of τ vs log η for solutions of nitrobenzene in benzene and in benzene + paraffin.

Curve II Graph of τ vs log η for the same solutions.

O Points for variation of temperature.

Δ Points for variation of viscosity at constant temperature.

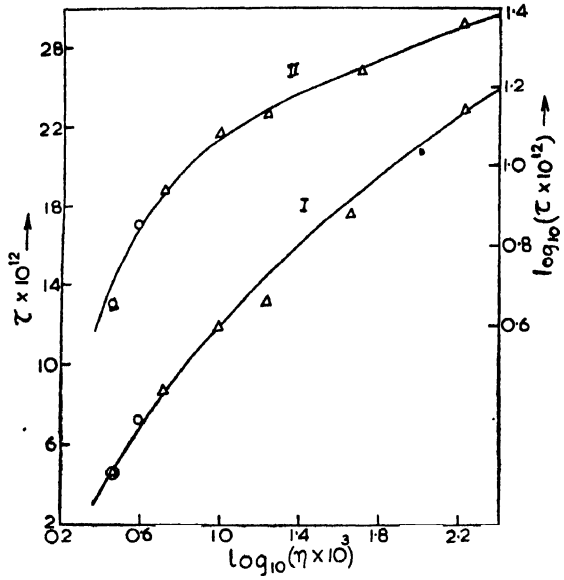

Fig. 4c. Curve I Graph of τ vs log η for solutions of nitrobenzene in hexane and in hexane + paraffin.

Curve II Graph of log τ vs log η for the same solutions.

O Points for variation of temperature.

Δ Points for variation of viscosity at constant temperature.

non-linearity of the curves log τ vs log η at higher viscosity values, the value of the inclination of the tangent at any point on the curve which measures E_τ/E_η decreases with increasing viscosity. All these considerations are applicable in the case of solutions in pure solvents when the viscosity is varied by changing the temperature.

It is thus seen that the equation (3) fairly represents the variation in τ/η. values over a wide range of temperature, whereas the values of τ/η obtained from the Debye relation

$$\tau = \frac{4\pi\eta a^3}{kT} \tag{4}$$

should always decrease with increasing temperature, which is not observed. Moreover, according to equation (4), for the same polar molecule in two solutions of different viscosities, τ_1/τ_2 should be equal to η_1/η_2 at a constant temperature. The present experimental results and those of previous workers (Jackson and Powles, 1946; Whiffen and Thompson, 1946) show that for widely different viscosities of the solutions, the relation (4) does not hold good. These discrepancies probably arise from the fact that the macroscopic viscosity (η) has been used in equation (4) in place of the internal viscosity.

(c) *Calculation of the radius of the rotor*

Using the value of τ/η obtained experimentally, the values of radius of the rotor as calculated by using equation (4) are given in Table V.

TABLE V

Solution in	T°K	a^3 in Å^3
CCl_4	343	6.5
C_6H_6	333	7.6
C_6H_{14}	274	5.5

The value of a^3 calculated from the density of nitrobenzene is 40.6 Å^3. Even allowing for free space the reduced value would be much larger than the value of a^3 given in Table V. As the radius of the spherical rotor comes out to be much smaller than the size of the actual molecule computed also from the chemical bond data, it is difficult to identify the rotor with the whole molecule. However, one may be tempted to identify the rotor with the NO_2 group in the phenyl ring. Though it is known that the NO_2 group is in the plane of the benzene ring, the NO_2 group may acquire a slight moment directed away from the plane in solutions in various solvents (Jenkins, 1936). But whether this may cause the NO_2 group to rotate is still to be seen and for this purpose investigations on the dielectric loss in a series of substituted nitrobenzenes in solutions in different nonpolar solvents have been undertaken.

(d) *Debye expression for dielectric loss as a function of viscosity of the solution*

The Debye expression given in equation (1) depends besides other quantities, on the value of the expression $\omega\tau/1+\omega^2\tau^2$, which for $\omega\tau \gg 2$ can be approximated by $\frac{1}{\omega\tau}$ $e^{-\frac{1}{\omega^2\tau^2}}$ to a good degree of accuracy. Combining the equations (1), (3) and (5) the following expression for tan δ as a function of η is obtained,

$$T.\tan\delta = \frac{P}{\eta^\gamma} e^{-Q/\eta^{2\gamma}} \qquad \ldots (6)$$

where $P = \frac{4\pi Nc\mu^2}{27k\alpha\omega} \cdot \frac{(\epsilon+2)^2}{\epsilon}$, $Q = \frac{1}{\alpha^2\omega^2}$ and $\gamma = E_\tau/E_\eta$. When $\gamma = 1$ and η is large the equation (6) becomes $T \tan\delta \approx P/\eta$ which may also be written as $T.\tan\delta \approx P \cdot e^{-2.303 \log_{10}\eta}$. The experimental results tally with the equation as discussed in Soc. (a). In the case of solutions with higher values of viscosity, since γ decreases with increase of viscosity, the value of $T.\tan\delta$ would not decrease as rapidly

as would have occured if γ were equal to 1. This is also in accordance with experimental results. Thus it may be concluded that within certain limitations the dependence of tan δ on viscosity may be described by the Debye expression.

(c) *A method for the determination of the dipole moment* (μ).

Incidentally, the equation (6) provides a rough method for the determination of μ of polar molecule. Equation (6) may be written in the form

$$\log_{10}(T \tan \delta \cdot \eta^{\gamma}) = \log_{10} P - \frac{Q}{\eta^{2\gamma}} \cdot \log_{10} e \qquad (7)$$

For a constant value of γ, which generally lies between 0.9 and 1.0 within viscosity limit of 1.3c.p., the graph of log (T tan $\delta \cdot \eta^{\gamma}$) vs $\frac{1}{\eta^{2\gamma}}$ would be a straight line from whose intercept and inclination the value of μ can be calculated from relations given in equation (6). Such graphs have been shown in the case of solutions in C_6H_6 and in CCl_4 in Figs. 5*a* and 5b for γ values 1.0 and 0.9 respectively. The

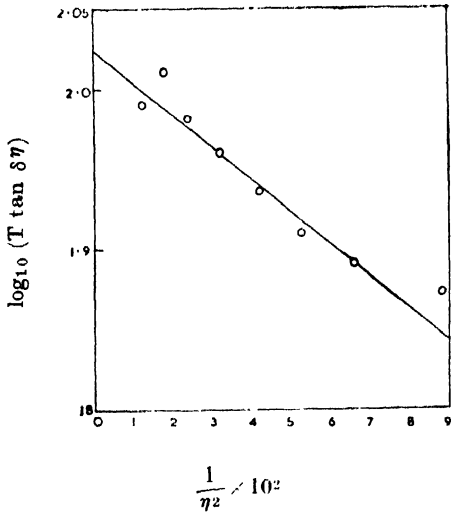

Fig. 5a. Graph of log (T tan $\delta.\eta^{\gamma}$) vs $\frac{1}{\eta^{2\gamma}}$ for solution in benzene with γ = 1.0.

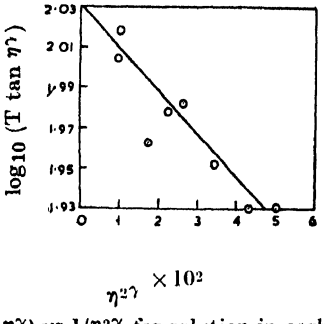

Fig. 5b. Graph of log (T tan $\delta.\eta^{\gamma}$) vs $1/\eta^{2\gamma}$ for solution in carbontetrachloride with γ = 0.9.

value of μ calculated from the graphs are given in Table VI. The literature value is included for comparison.

TABLE VI

Solution in	μ in Debye Unit calculated	μ in Debye Unit Literature value
CCl_4	3.90	3.98
C_6H_6	3.92	

The value of μ obtained by the above method is smaller than the value of μ used in the present investigation by about 2%. Considering the various approximations involved, this may be regarded as satisfactory. If this method is applicable in general remains to be seen. For this purpose the investigations are being extended to a large number of polar organic compounds.

ACKNOWLEDGMENT

The authors express their grateful thanks to Mr. A. K. Sarkar, Workshop Superintendent, Indian Association for the Cultivation of Science, for help in fabricating the wave guide components used in the present experiment.

REFERENCES

Chau, J. Y., Le Fevre, R. W. and Tardif, J., 1957, *J. Chem. Soc.* Part II, pp. 2293.

Cripwell, F. J. and Sutherland, G. B. B. M., 1946, *Trans. Farad. Soc.*, 42A, 149.

Gopala Krishna, K. V., 1957, *Trans. Farad. Soc.*, **53**, 767.

Hall, H. W., Halliday, I. G., Johnson, W. A. and Walker, S., 1946, *Trans. Fard. Soc.*, **42A**, 136.

Jackson, W., 1946, *Trans. Farad. Soc.*, 842A, 15.

Jackson, W. ad Powles, J. G., 1946, *Trans. Farad. Soc.*, **42A**, 136.

Jenkins, H. O., 1936, *J. Chem. Soc.*, p.862

Rajan, S., 1956, *Curr. Sc.*, **23**, 238.

Whiffen, D. H. 1946, *Trans. Frad. Soc.*, **42A**, 156.

Whiffen, D. H., 1950, *Trans. Farad. Soc.*, **46**, 13.

Whiffen, D. H. and Thompson, H. W., 1946, *Trans. Farad Soc.*, **42A** 114, 122.